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First Technical Report

1st October 1992 - 30th November 1992

Principal Investigator: Dr Robin John Neat

LITHIUM POLYMER BATTERIES FOR SPACE POWER APPLICATIONS

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Executive Summary

This report documents the results of the work performed by AEA Technology under contract number F61708-92-C0039 over the period 1st October 1992 to 30th November 1992 and represents deliverable item 002.

The US Air Force is undertaking a number of projects aimed at developing new and improved secondary battery systems for the provision of baseload power in satellites.

This project has the objectives of evaluating the Lithium Polymer Battery (LPB), developed by AEA Technology, against a GEO satellite duty cycle, and subsequently developing the battery system with a view to improving on its performance.

A Mark I LPB cell has been defined as a lithium metal anode, lithium-ion conducting polymer electrolyte (PEO_{12}:$LiClO_4$) and a composite cathode based on V_6O_{13}. The chosen operating temperature is 120°C.

The space power duty cycle employed for the evaluation is a fixed discharge time of 72 minutes and a total charging time of 10 hours.

In this report evaluation results are presented covering the variables of depth of discharge (DoD) and discharge current density, using a cell cathode capacity of 2.5 mA h cm^{-2}.

The energy losses on repeated discharge/charge cycling are approximately 2.8% for 20% DoD over 50 cycles, 3.1% for 40% DoD over 40 cycles and 0.5% for 60% DoD over 15 cycles. Cells discharged to 80% and 100% DoD were unable to sustain the required current for the full 72 minutes.

Evaluation of many of the cells reported on here continues and results will be updated in the second technical report.

CONTENTS

1. Objectives of Research and Statement of Work

1.1 Introduction and Objectives

The provision of baseload power for space vehicles remains a major technological challenge. The most common solution, used exclusively in satellites, is the combination of photo-voltaic cells and secondary batteries. The performance of current state-of-the-art secondary batteries is poor; they are bulky and heavy.

It is clear that an improvement in secondary battery technology would provide a significant payoff in terms of performance, survivability and affordability. Currently the majority of satellites fly with Ni-Cd batteries. These suffer from being both heavy and bulky (energy density 25-30 W h kg^{-1} and 50-60 W h $litre^{-1}$).

The US Air Force is undertaking a number of projects aimed at developing new and improved secondary batteries for satellite power applications. This report documents work carried out by AEA Technology under contract F61708-92-C0039 which has the object of evaluating the AEA-developed Lithium Polymer Battery against the GEO satellite duty cycle, and subsequently undertaking a development program to improve the battery's performance.

The Lithium Polymer Battery (LPB) is an all solid-state system which combines a lithium ion conducting polymer electrolyte with two lithium ion reversible electrodes. The polymer electrolyte also acts as a mechanical separator for the two electrodes. In most cases the anode is a metallic lithium foil. The cathode is typically a reversible intercalation compound such as V_6O_{13} or TiS_2 in the form of a composite backed by a metal foil current collector. LPB cells are fabricated by lamination of the three component layers; lithium foil, polymer electrolyte and composite cathode. The LPB concept has a number of advantages based on the all-solid-state construction; high energy density, high power density, good shelf life and excellent safety characteristics.

This project is the first phase of a three-phase program designed with the objective of translating the promise of the LPB technology into prototype battery units.

1,2 Statement of Work

The statement of work (SOW) specifies the requirements for AEA Technology to evaluate the lithium polymer battery against the GEO satellite duty cycle, and subsequently undertaking a development program to improve the battery's performance. AEA Technology is performing three work packages in order to achieve the objectives of the program. These are illustrated in the work

breakdown structure in Figure 1.

Work package 1 will be performed from the program start for nine (9) months, although the electrical testing phase may be allowed to continue if results are promising. Work package 2 will run from month nine (9) to month twenty three (23) and is designed to follow on from work package 1. Work package 3 will be performed from month three (3) to month (21) and is designed to run concurrently with work packages 1 and 2.

Work Package 1.

AEA Technology will draw up a specification for the Mark I LPB which will be the most advanced version of the V_6O_{13}-based LPB at the start time of the contract. AEA Technology will use its facilities in the Lithium Battery Section of the Applied Electrochemistry Department to test the cycle performance of the Mark I LPB cell against the following variables: a range of depths of discharges (20%, 40%, 60%, 80% and 100%) of the cell's theoretical capacity; a range of cathode capacities (1.0, 1.5, 2.0, 2.5 and 3.0 mA h cm^{-2}); a range of discharge current densities (0.2, 0.5, 1.0 and 2.0 mA cm^{-2}), and different charging techniques (constant current, constant potential and mixed mode). The results of the testing will be presented as a benchmark performance and included in a technical report. The length of cycle testing will be constrained by the testing equipment available.

Work Package 2.

AEA Technology will study the cycling performance of the Mark I LPB in which V_6O_{13} is replaced as the active cathode material by: $LiMn_2O_4$ and related spinels (e.g. $Li_2Mn_4O_9$); MnO_2; V_2O_5 and TiO_2. Following initial evaluation of the compounds listed above, AEA Technology will attempt to optimise the Mark I cell configuration and/or composition to yield cycle performance which is superior to that of the V_6O_{13}-based Mark I cell. The testing and evaluation of these alternative cathode material cells will be restricted to combinations of parameters (i.e. depth of discharge, current density and cathode capacity) for which it is possible to predict superior performance.

Work Package 3.

AEA Technology will apply several investigative analytical techniques which it has developed, or is in the process of developing, to identify LPB performance limiting phenomena. AEA Technology will build LPB cells which contain a reference terminal and use three terminal

a.c. impedance analysis to monitor changes in the overall cell impedance, the lithium/electrolyte impedance and the electrolyte/cathode impedance during cycling. Using the resulting data AEA Technology will attempt to modify the LPB cell configuration and/or composition to remove or reduce any identified performance limiting factors. AEA Technology will section LPB after testing, and use a scanning electron microscope to examine the physical condition of the cell. EDX analysis will also be used to examine the chemical composition of the cell layers. Using the resulting data AEA Technology will attempt to modify the LPB cell configuration and/or composition to remove or reduce any identified performance limiting factors. AEA Technology will use a post test X-ray diffraction technique to examine the crystal structure of the active cathode material. Using the resulting data AEA Technology will attempt to modify the LPB cell configuration and/or composition to remove or reduce any identified performance limiting factors.

1.3 The Current Report

The first technical report documents the work performed over the period 1st October 1992 to 30th November 1992 and is deliverable item 002. The report covers the first two months of effort under Work Package 1.

2. Status of Research Effort - Progress against Objectives

2.1 Status of Work in Work Package 1

2.1.1 Definition of Mark I LPB cell

Following a review of the internal performance data available at AEA Technology, we have defined the Mark I LPB cell as follows:

Anode

The anode is lithium metal foil which is commercially available. AEA Technology procures the lithium as 10 cm wide 100 μm thick foil. This thickness of foil gives a vast excess of lithium. The exact amount depends on the capacity of the composite cathode; for a cell that contains a cathode with 2.5 mA h cm^{-2} there is a five fold excess; which rises to a thirteen fold excess for a 1.0 mA h cm^{-2} capacity cell. This thickness of foil is used for pragmatic reasons (i.e. it is easy to handle and thinner foils are not readily available and are very expensive). It is, of course, recognised that this amount of lithium reduces the energy density of the system. This will be addressed in phase II of the program.

Cathode

The cathode is a composite based on V_6O_{13} and has the composition 45 vol. % V_6O_{13}, 5 vol. % ketjen black carbon and 50 vol. % PEO-$LiClO_4$ ([EO units] / [Li] =12). The composite cathode is backed onto a nickel foil current collector. The binder is the polymer material used in the electrolyte and will be termed the catholyte. Ketjen black carbon is added as an electronic conductivity enhancer. The ratio of these components in weight % is V_6O_{13} 68 %, carbon black 4 % and catholyte 28 %.

Electrolyte

The Mark I LPB cell utilises a polymer electrolyte prepared from a high molecular weight polyethylene oxide (WSR 301) and lithium perchlorate. The polymer electrolyte has a ratio of ethylene oxide units to lithium of 12 ([EO units] / [Li] =12), and is normally written as PEO_{12}:$LiClO_4$. The electrolyte phase contains no plasticisers.

Operating Temperature

Previous work at AEA Technology has shown that the Mark I cell will operate over the range 80°C - 140°C; although the performance is not independent of temperature.

For this project we have chosen 120°C as the cell operating temperature.

Energy Density

The energy density of the LPB system is very sensitive to cathode capacity. For our Mark I 40 cm^2 test cell with a cathode capacity of 2.5 mA h cm^{-2} we obtain close to 100% of the theoretical capacity (i.e. 100 mA h) for discharge rates of C/5 and lower. The average discharge voltage is ~ 2.2 V giving an energy of 220 mW h. The weight of such an unpackaged Mark I cell is ~ 2.56 g, and therefore the corresponding energy density is ~ 85 W h kg^{-1}. It should be noted that at the present time over half the cell weight is due to the nickel foil current collectors, there is an excess of lithium and there is a large redundancy of materials. The table below shows the projected energy density numbers for optimised Mark I V_6O_{13}-based test cells with different cathode capacities, assuming 100 % depth of discharge.

Cathode Capacity / mA h cm^{-2}	Energy Density / W h kg^{-1}	Vol. Energy Density/ W h $liter^{-1}$
1.0	140	158
1.5	169	204
2.0	197	249
2.5	228	297
3.0	254	340

NB all numbers quoted are based on real components and assume a cell with 50μm lithium foil, 85 μm PEO-LiClO4 electrolyte and a 10μm aluminium current collector. Numbers are for unpackaged laminate only.

2.1.2 Experimental

Lithium Foil

The lithium foil used was 100 μm battery grade (FMC Lithium Division). This was cold rolled onto a nickel foil current collector.

Composite Cathode

V_6O_{13} was prepared in-house by the thermal decomposition of ammonium metavanadate in

an argon atmosphere, and dried for 8 hours under vacuum at 50 °C prior to use. The PEO, carbon and lithium perchlorate were dried under vacuum, at 50 °C, 100 °C and 130 °C respectively, before use. Composite cathodes were prepared using the following procedure. 17.44 g of V_6O_{13} and 1.1 g of ketjen black carbon (EC 300 N, Akzo) were ball-milled for 2.5 hours in a sealed pot containing 80 cm^3 of 1,1,1-Trichlorethane (99+ %, < 0.005 % water, Aldrich) and two drops of a wetting agent, span 80 (Fluka). 6.00 g of PEO (WSR 301, Aldrich) were then added to the mix and the pot was returned to the ball-mill. After 10 minutes 1.21 g of $LiClO_4$ (A.C.S. reagent, Aldrich) dissolved in 230 cm^3 of acetonitrile (99+%, < 0.005% water, Aldrich) was added, and the mix was ball-milled for a further hour. After leaving the mix to stand for approximately 1 hour (to aid degassing) it was cast in the Harwell dry room (T=20 °C, dew point temperature -30 °C) onto a nickel foil (14 μm, Inco Alloys) using a small doctor blade coater with a blade gap of 1.5 mm. The coating was left to dry (initially under a fume hood) for a total of 16 hours. The capacity of the resulting composite cathode was ~ 2.5 mA h cm^{-2}.

Polymer Electrolyte

The polymer electrolyte, PEO_{12}:$LiClO_4$, was prepared by dissolving 48 g of PEO (WSR 301, Aldrich) and 9.68 g of $LiClO_4$ (A.C.S. reagent, Aldrich) in 2 litres of acetonitrile (99+ %, < 0.005 % water, Aldrich) and ball-milling for 2 hours. After degassing the electrolyte solution was cast onto a silicone release paper using a blade gap of 1.5 mm. The thickness of the dried polymer electrolyte film was ~ 26 μm.

Cell Construction

All LPB cell construction was carried out in the Harwell dry room. In the initial fabrication step two layers of the polymer electrolyte film (total thickness ~ 54 μm) were laminated to the composite cathode, using a combination of heat and pressure. This was followed by the lamination of the lithium to form the complete cell. After connection of electrode tags the cells were vacuum packaged and placed in an oven at 120°C. Prior to testing LPB cell a.c impedances were measured using a Solartron 1254 frequency response analyser in conjunction with a Solartron 1286 electrochemical interface over the frequency range 65 kHz to 1.0 Hz.

2.1.3 Cell Testing Parameters

The initial space power duty cycle agreed for this project consists of a fixed discharge time of 72 minutes and a total charging time of 10 hours. In order to undertake Task 1.1 we have chosen a cathode capacity of 2.5 mA h cm^{-2}. This gives a theoretical capacity of 100 mA h for the

40 cm^2 Mark I LPB cell. The discharge current has been varied to correspond to DoDs of 20%, 40%, 60%, 80% and 100% as indicated in Table I below.

Table I

DoD	Discharge current / mA	Current density / mA / cm^2	Discharge rate
20%	16.7	0.42	C/6
40%	33.3	0.83	C/3
60%	50.0	1.25	C/2
80%	66.7	1.67	C/1.5
100%	83.3	2.01	C/1.2

Based on previous experience a 'mixed' mode of charging has been initially chosen.This consists of a constant current charge to 3.25 V followed by a potentiostatic hold at 3.25 V such that the total charge time is 10 hours. A lower voltage limit of 1.5 V has been used to determine the end of life in all cases.

For each electrical evaluation, the testing software employed by AEA Technology records, cell voltage, cell current, elapsed time and cell temperature. The cycle performance data will be presented in two forms; discharge energy versus cycle number and end of discharge voltage versus cycle number (see for example Figure 3). In additional, individual discharge cycles will be illustrated by showing discharge time versus cell voltage. The latter format enables one to compare the shape of the discharge curve with cycling, and can be useful in indicating the onset of structural changes within the active cathode material.

A.c. impedance data are obtained for every cell prior to testing and again at the end of cycle life. This data will only be shown if it differs from that normally observed for the Mark I cell and illustrates changes in impedance, resulting from delamination or increased interfacial resistance for example, that could be used to explain a particular cell performance. The a.c. technique will be employed specifically in Task 3.1 of Work Package 3. The a.c. impedance for a typical LPB Mark I cell is shown in Figure 2.

2.1.4 Results and Discussion

This technical report documents the work performed during the first two months of effort under Task 1.1 of Work Package 1. The performance of the Mark I cell under the space duty cycle as a function of depth of discharge is an ongoing task. The majority of LPB cells described in the

results section below remain on test. An update on their performance will be provided in the next technical report.

20% Depth of Discharge

The cycling performance data for a group of 3 Mark I LPB cells discharged to 20% depth of discharge are given in Figure 3. After 50 cycles there is less than a 3% loss in the discharge energy, while the end of discharge voltage has decreased by ~ 0.07 V. The 1st, 20th and 50th discharge cycles for cell P003 are shown in Figure 4. This illustrates that the discharge occurs on two voltage plateaux; the first at ~ 2.75 V is associated with the insertion of 1 lithium into the V_6O_{13} structure to form the phase LiV_6O_{13}. As a consequence of the phase rule when two compounds (in this case V_6O_{13} and LiV_6O_{13}) coexist during the discharge the cell voltage remains approximately constant, resulting in an observed plateau. The final composition of the cathode material at the end of discharge is $Li_{1.6}V_6O_{13}$. A comparison between the 1st and 50th cycles indicates that the two plateaux have become less distinct. This is consistent with the onset of a gradual transformation in the V_6O_{13} structure in which there is a loss of crystallinity and the material undergoes a transition to an amorphous compound.

40% Depth of Discharge

Figure 5 shows the cycling performance data for a group of 3 Mark I LPB cells discharged to 40 % depth of discharge. For LPB cells P009 and P010 the energy loss over the first 40 cycles was approximately 3 %. A significant proportion of the observed decrease in the end of discharge voltage (~ 0.10 V) occurred during the initial 15 cycles. Although the first discharge of LPB cell P007 was very similar to those of LPB cells P009 and P010 the energy of the subsequent discharge cycles declined rapidly. The cell was removed from test after 25 cycles due to failure to discharge for the required 72 minutes above the cutoff voltage of 1.5 V. The discharge curves for the 1st, 20th and 40th (or final) cycles for LPB cells P010 and P007 can be compared in Figures 6 and 7. While LPB cell P010 exhibited a gradual loss of the voltage plateeau at ~ 2.75 V with cycle number this was not accompanied by the same large decrease in the discharge voltage (ultimately resulting in cell failure) observed for LPB cell P007. The a.c. impedance for LPB cell P007 after 25 cycles, Figure 8, showed a significant increase over the initial value. The behaviour of P007 illustrates the problem of cell-to-cell irreproducibility which is inherent in the hand construction methods employed.

60% Depth of Discharge

The first 15 cycles of performance data for 3 Mark I LPB cells discharged to 60% depth of discharge are given in Figure 9. After 15 cycles there is a ~ 0.5% loss in energy compared to the

initial discharge for LPB cells P012 and P013, whereas for P011 the energy has actually increased by 0.6%. It is interesting that the energy of the second discharge cycle for all three cells is higher than that of the first. A similar trend is observed for the end of discharge voltage. This may indicate a lowering of cell resistance during the first cycle. The 1st and 15th discharge curves for LPB cell P012 are shown in Figure 10. Some loss of the well-defined voltage plateaux has occurred consistent with a gradual transformation of the V_6O_{13} to an amorphous material.

Figure 11 illustrates a direct comparison between the cycling performance data for 20% (P003), 40% (P010) and 60% (P012) depth of discharge. As expected the discharge energy increases for a greater depth of discharge, while the end of discharge voltage is lower.

80% and 100% Depth of Discharge

The first discharge data for Mark I LPB cells cycling under 80% and 100% depth of discharge are shown in Figures 12 and 13. One consequence of the higher discharge rates (C/1.5 to C/1.2, see Table I) is that the utilisation of the V_6O_{13} is reduced such that the lower voltage limit of 1.5 V was reached before the required 72 minutes. Cathode utilisations of ~ 70% and ~ 50% were observed for the 80% and 100% depth of discharge respectively. These results indicate that for a Mark I LPB cell with cathode capacity of 2.5 mA h cm^{-2}, a depth of discharge of 70% represents the maximum attainable under the present duty cycle with a lower voltage limit of 1.5 V. The energy obtained during the first discharge of the Mark I LPB cells cycled under 80% and 100% depth of discharge is less than for LPB cells cycling at the lower 60% depth of discharge (~ 135 mW h). Our previous experience has indicated the rate performance (i.e. cathode utilisation) of the LPB cell is dependent on the cathode capacity (thickness). We would expect better high rate performance from a Mark I LPB cell with a thin cathode (~ 1.0 mA h cm^{-2}), although it will possess a lower theoretical energy density. Evaluation of Mark I LPB cells of this type are to be carried out in the next sequence of experiments.

2.1.5 Conclusions

For a Mark I LPB with cathode capacity 2.5 mA h cm^{-2}, tested under a space power duty cycle consisting of a 72 minute discharge and 10 hour mixed mode charge, the energy obtained on discharge increases with increasing depth of discharge, up to a level of 60%. The energy losses over the first 40-50 cycles are of the order of 3% for 20% and 40% depth of discharge. LPB cells discharged to 80% and 100% depth of discharge were unable to sustain the discharge current for the full 72 minutes. At the present time insufficient performance data exists to give a clear indication as to which depth of discharge is most likely to provide the cycle life required for GEO applications.

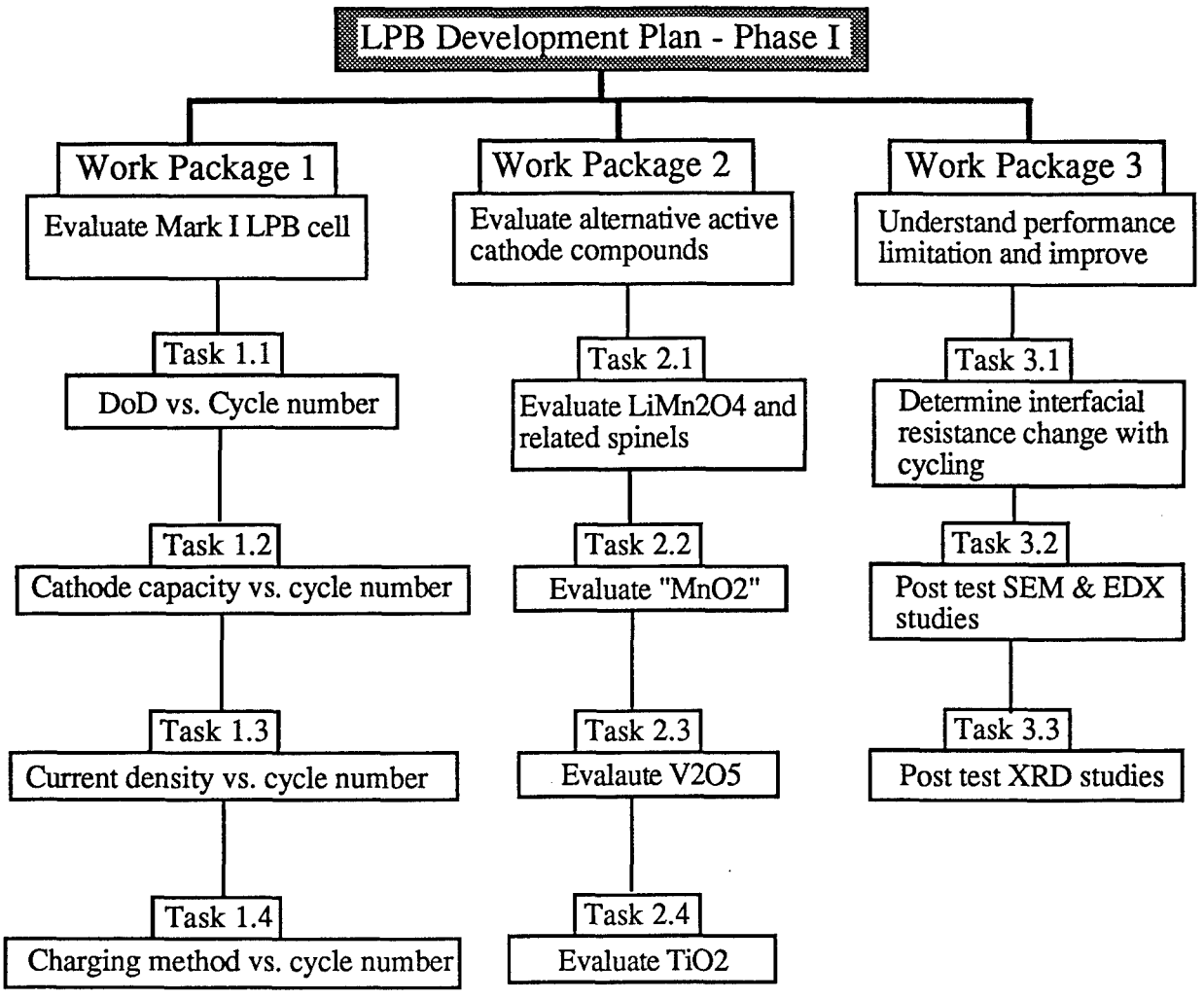


Figure 1 *Work Breakdown Structure.*

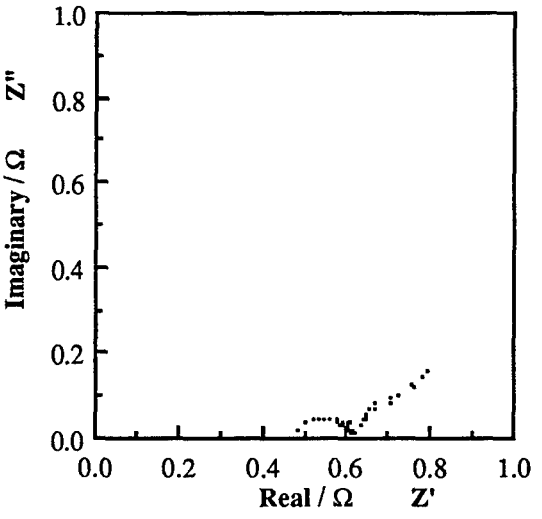
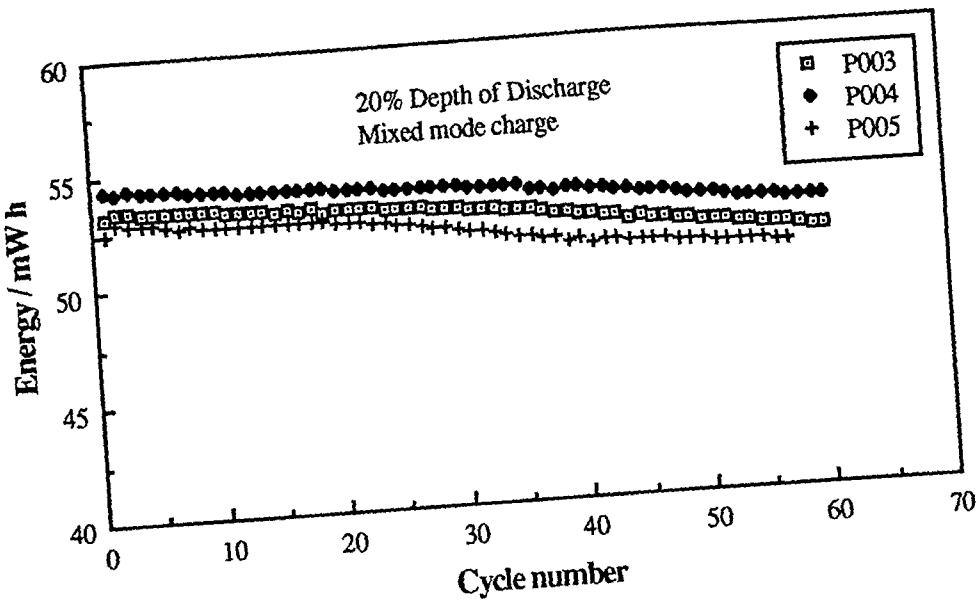


Figure 2 *Typical a.c. impedance for a 40 cm² Mark I LPB cell.*



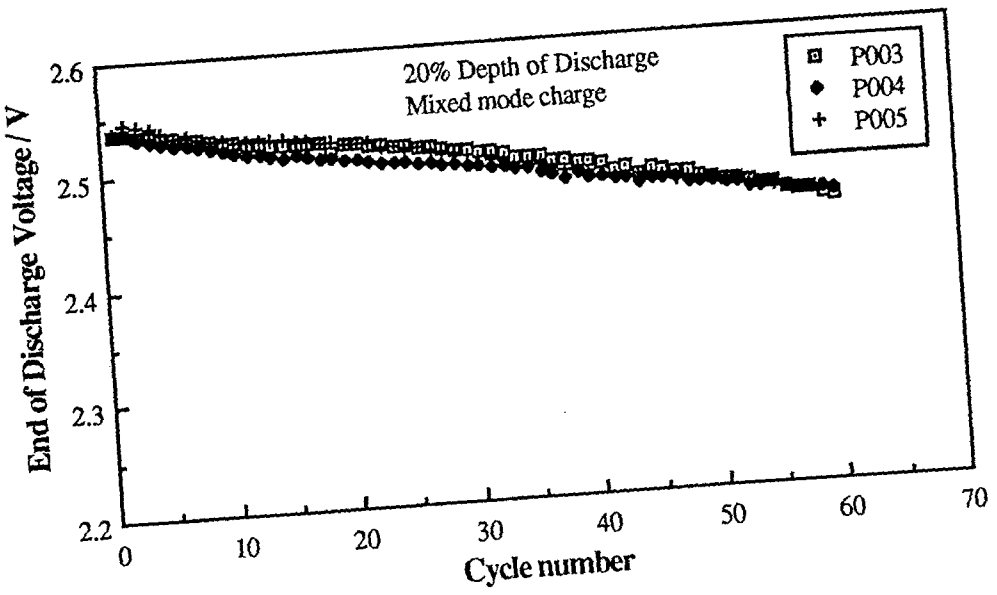
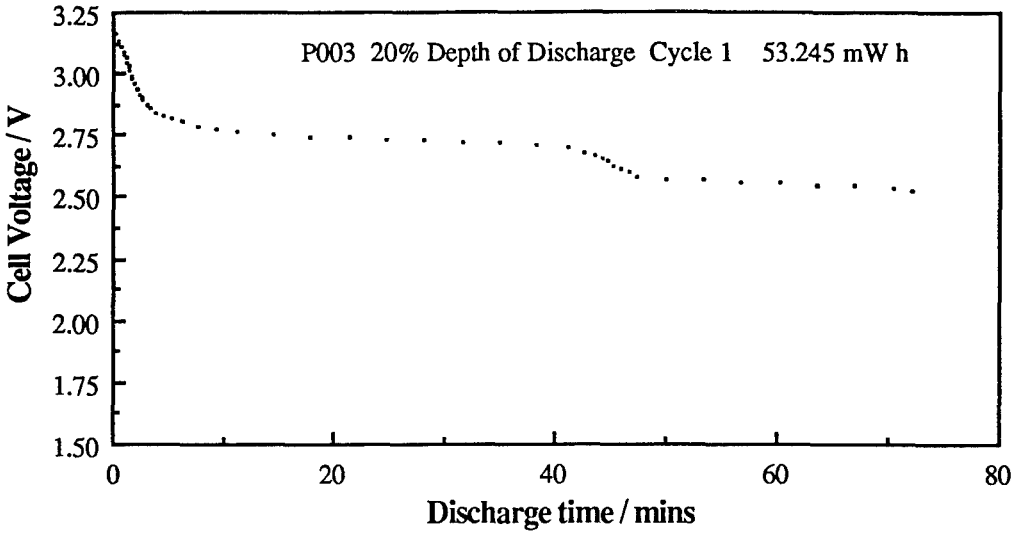
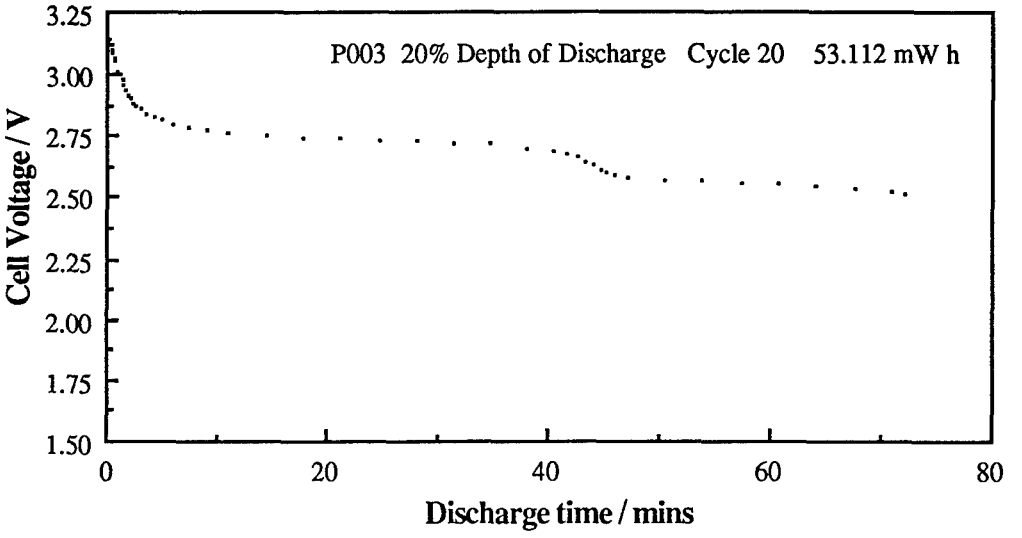


Figure 3 *Cycle performance data for the Mark I LPB cell at 20% depth of discharge.*





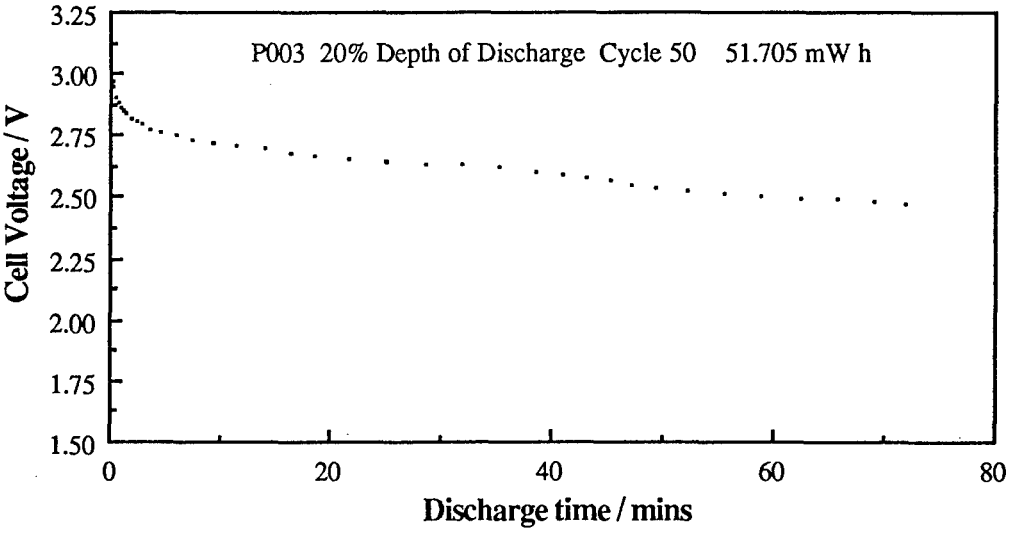


Figure 4 *1st, 20th and 50th discharge cycles for a LPB cell at 20% depth of discharge.*

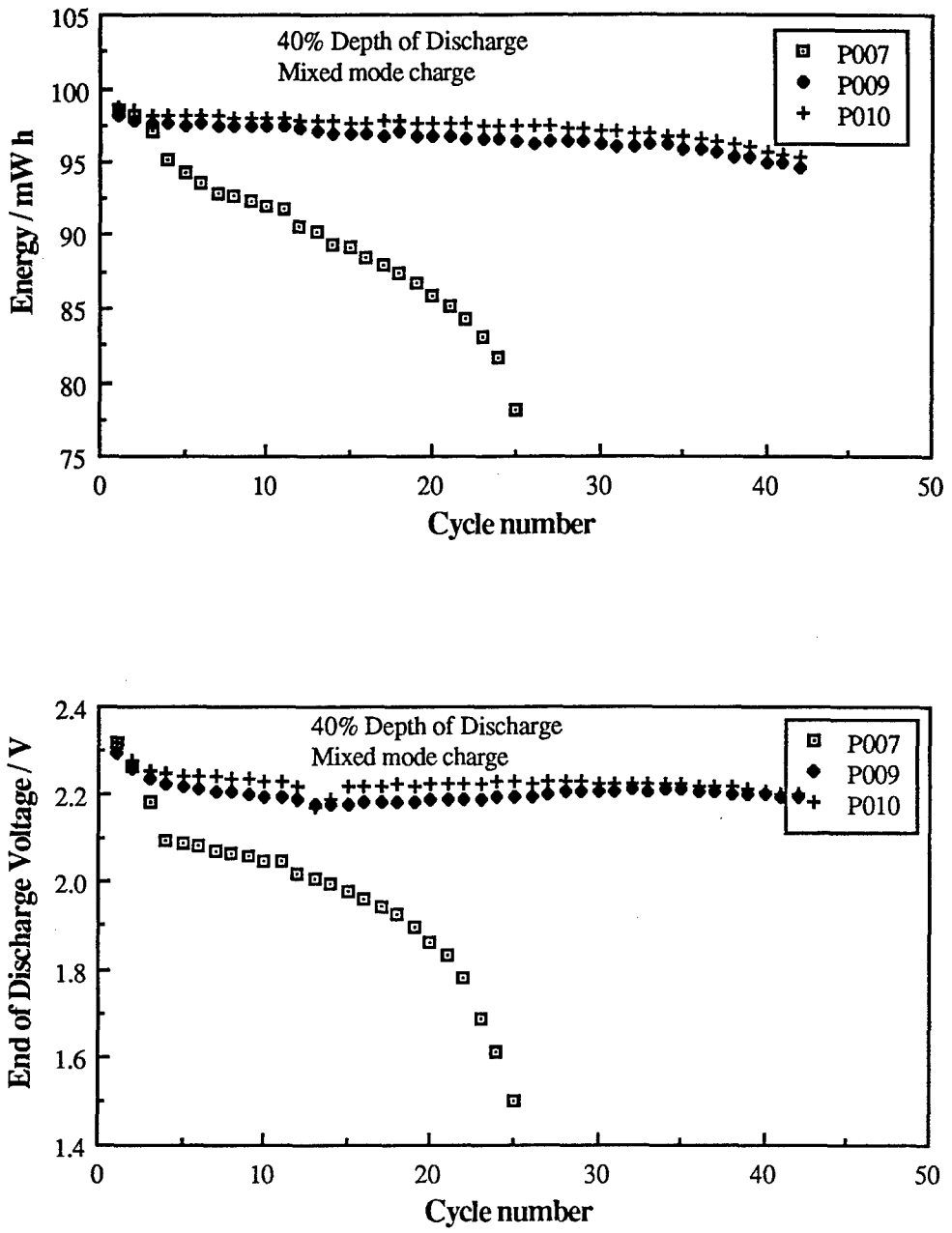
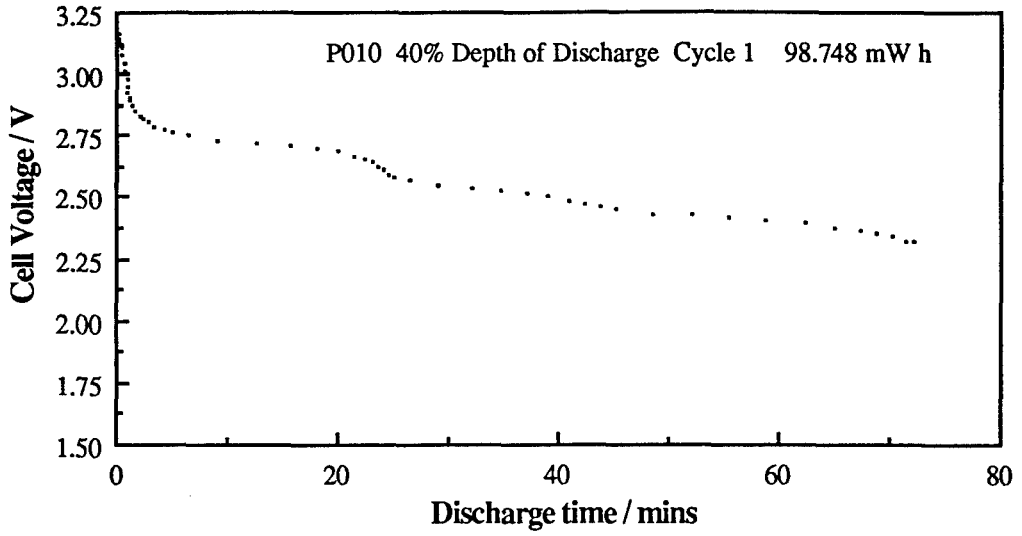
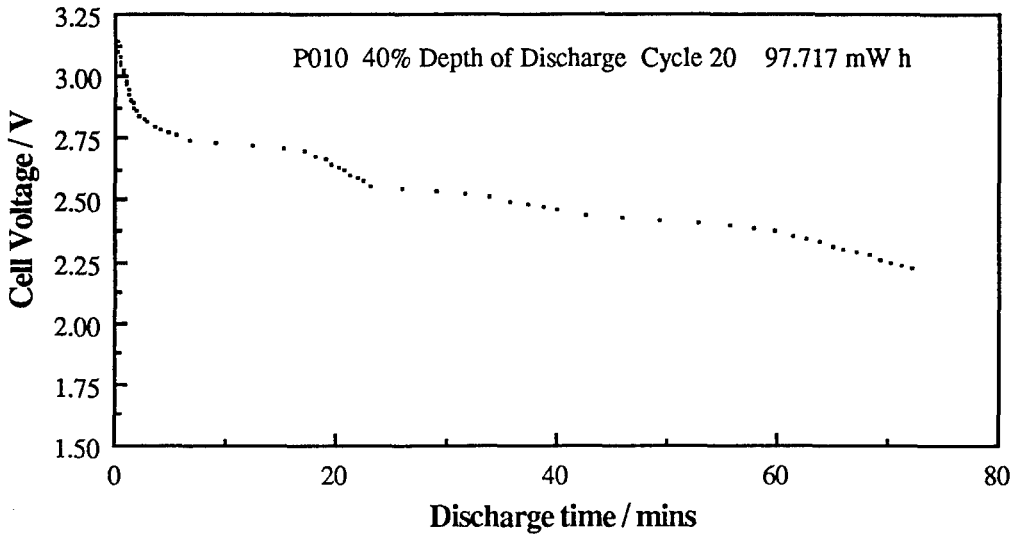


Figure 5 *Cycle performance data for the Mark I LPB cell at 40% depth of discharge.*





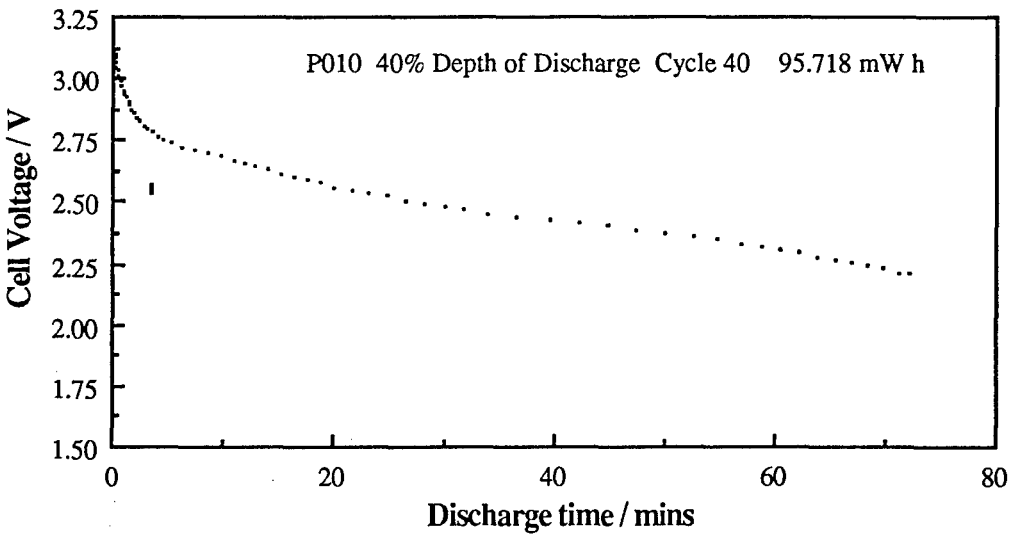
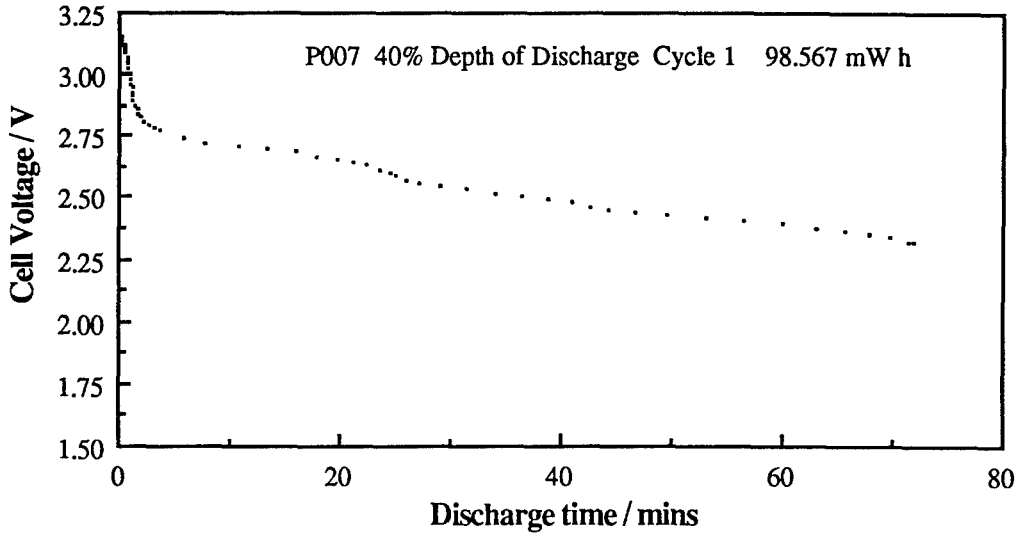
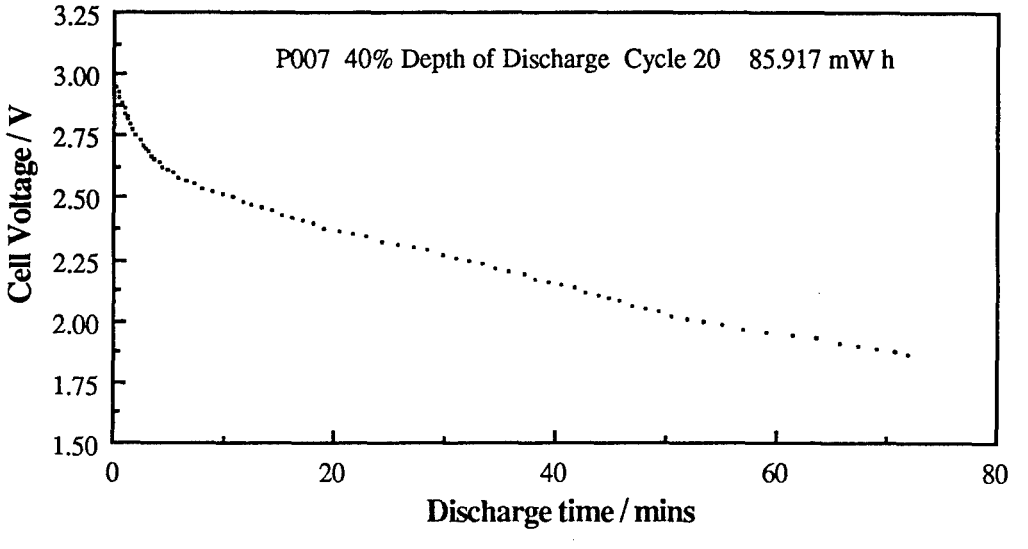


Figure 6 *1st, 20th and 40th discharge cycles for LPB cell P010 at 40% depth of discharge.*





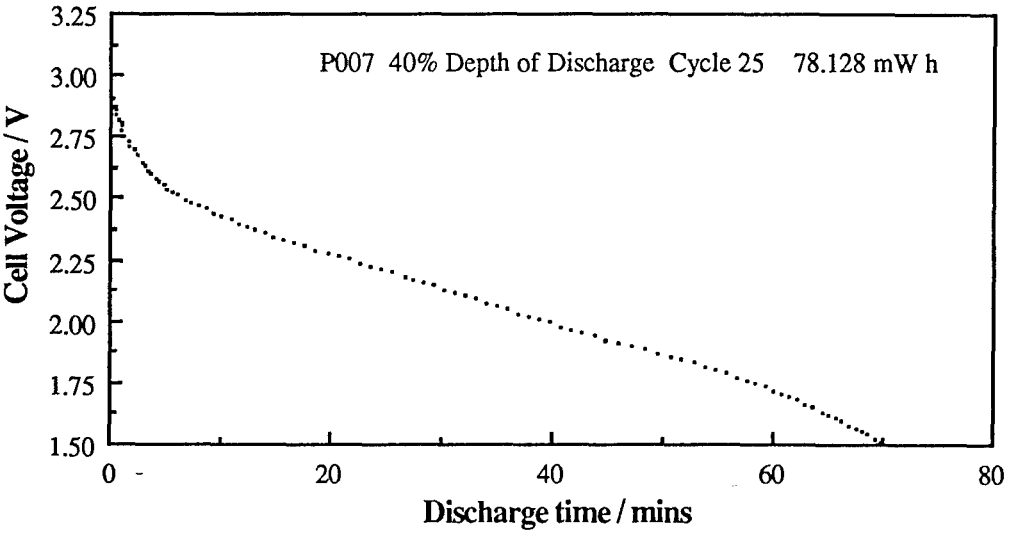


Figure 7 *1st, 20th and 25th discharge cycles for LPB cell P007 at 40% depth of discharge.*

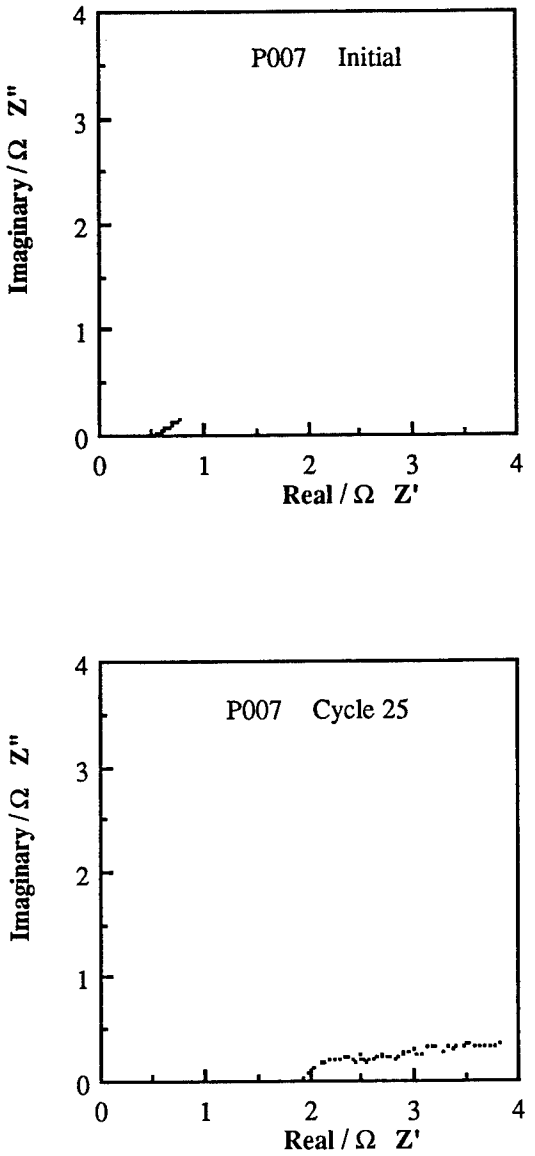


Figure 8 *Initial and final a.c. impedance data for LPB cell P007.*

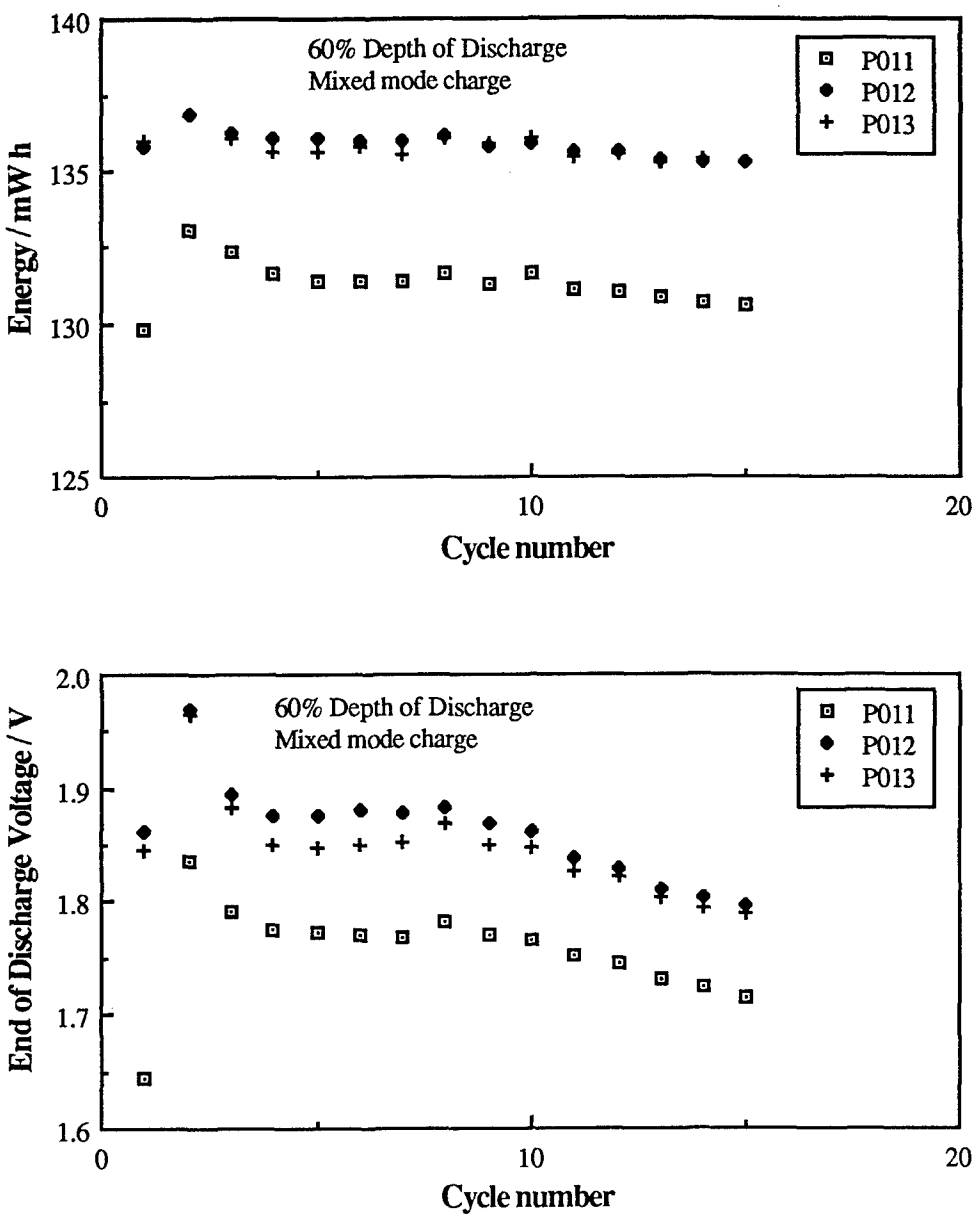
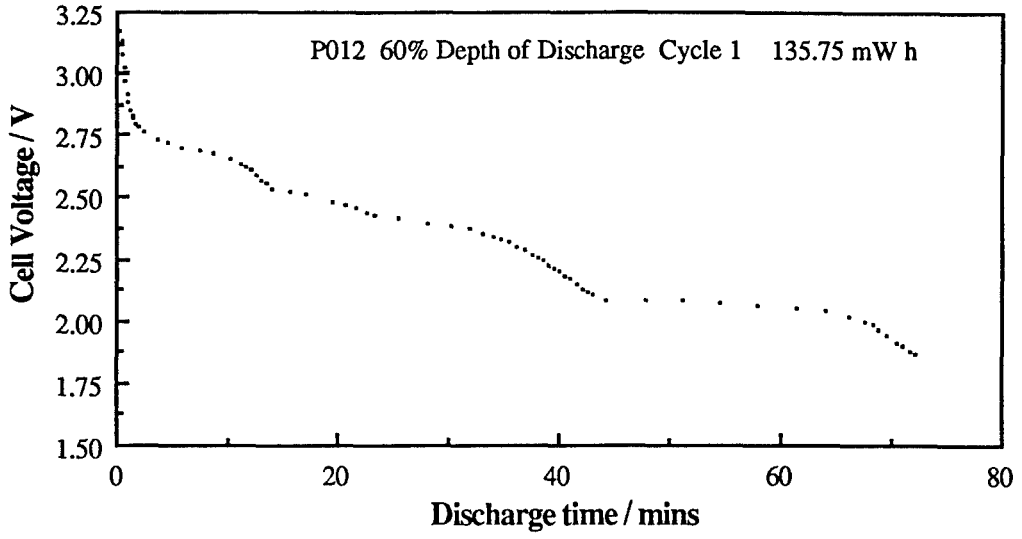


Figure 9 *Cycle performance data for the Mark I LPB at 60% depth of discharge.*



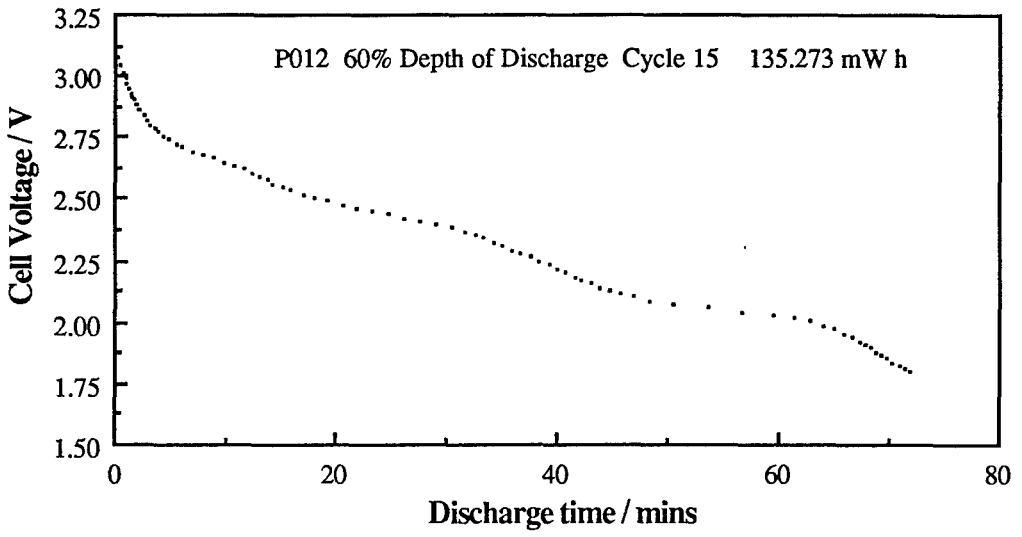


Figure 10 *1st and 15th discharge cycles for LPB cell P012 at 60% depth of discharge.*

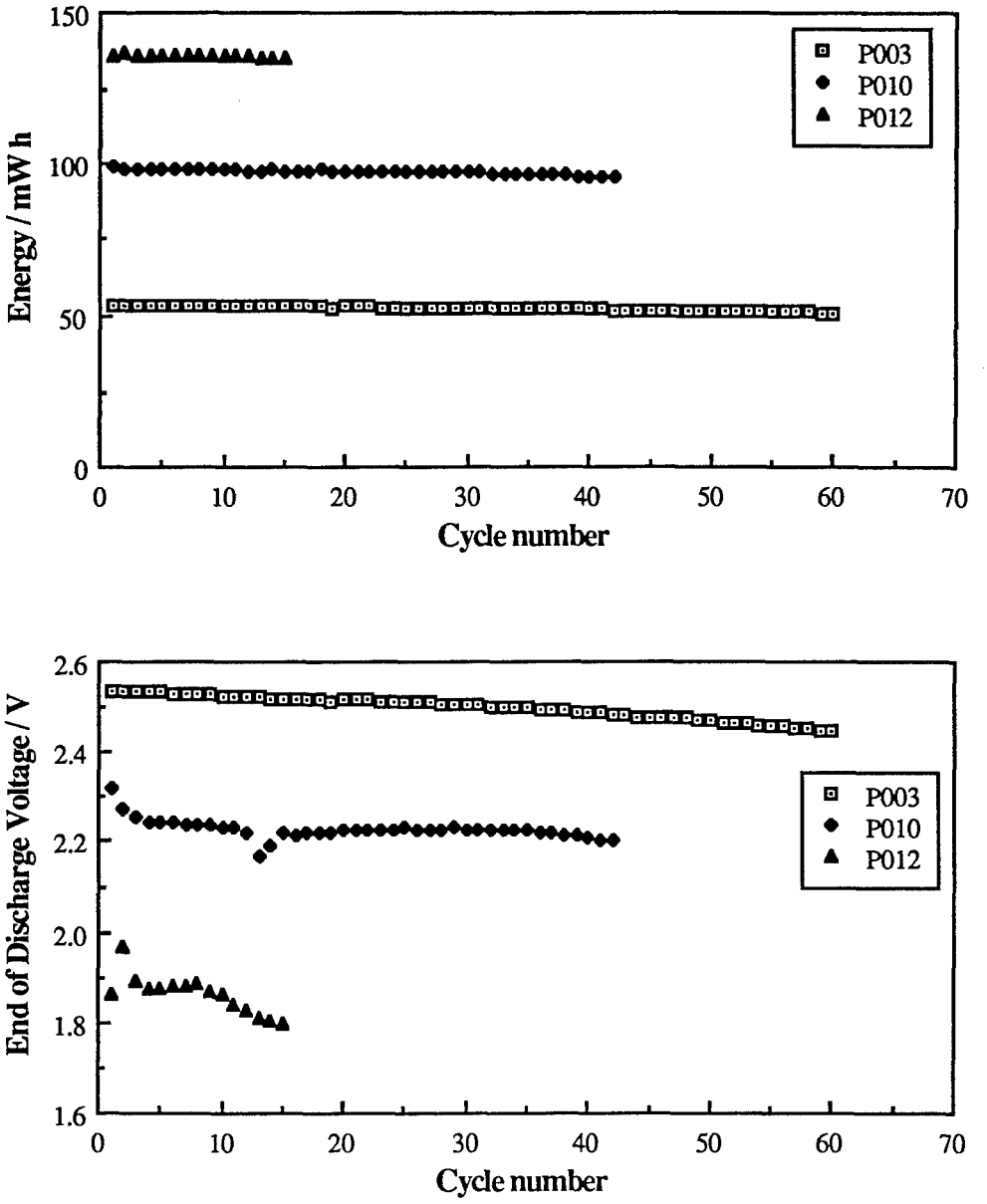
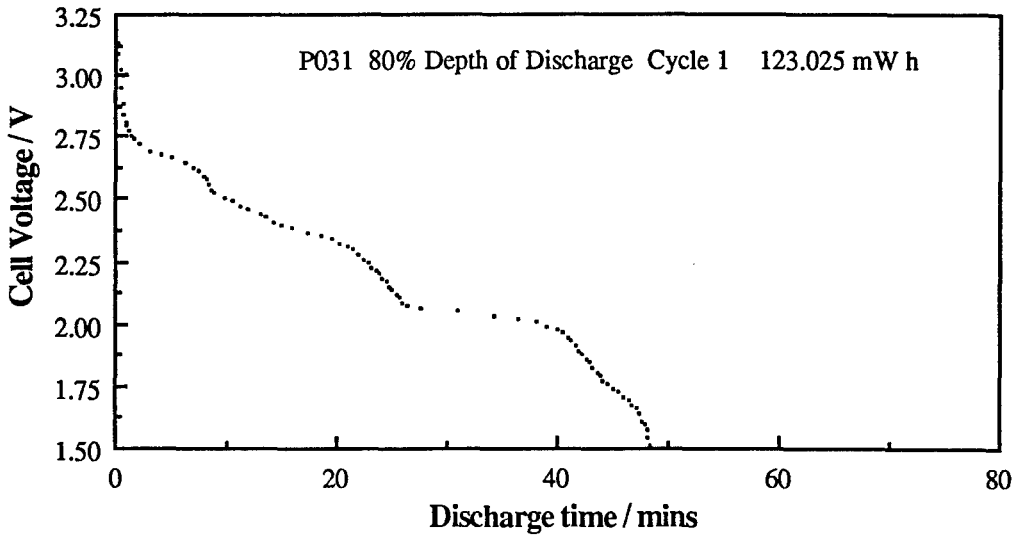
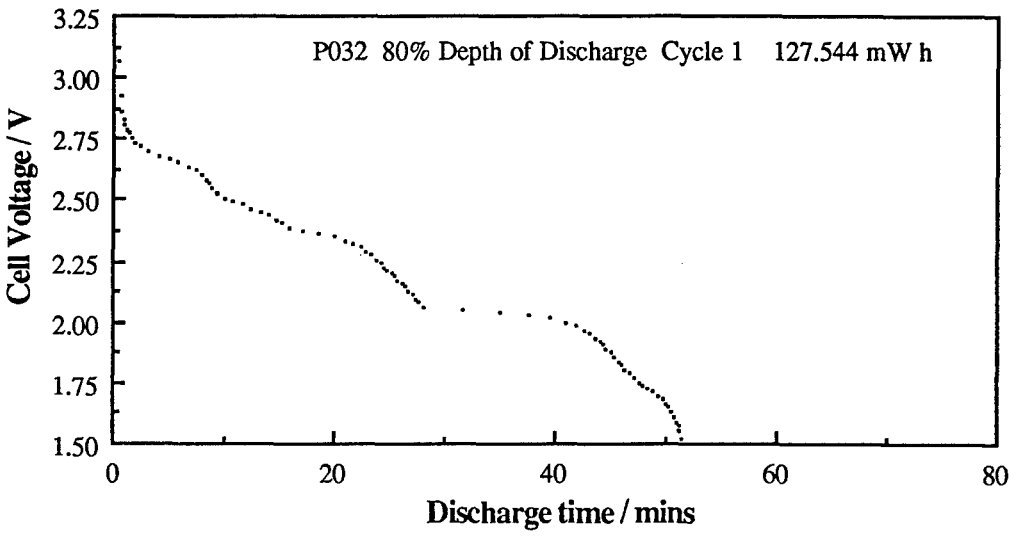


Figure 11 *Comparison of cycle performance data for 20%, 40% and 60% depth of discharge.*





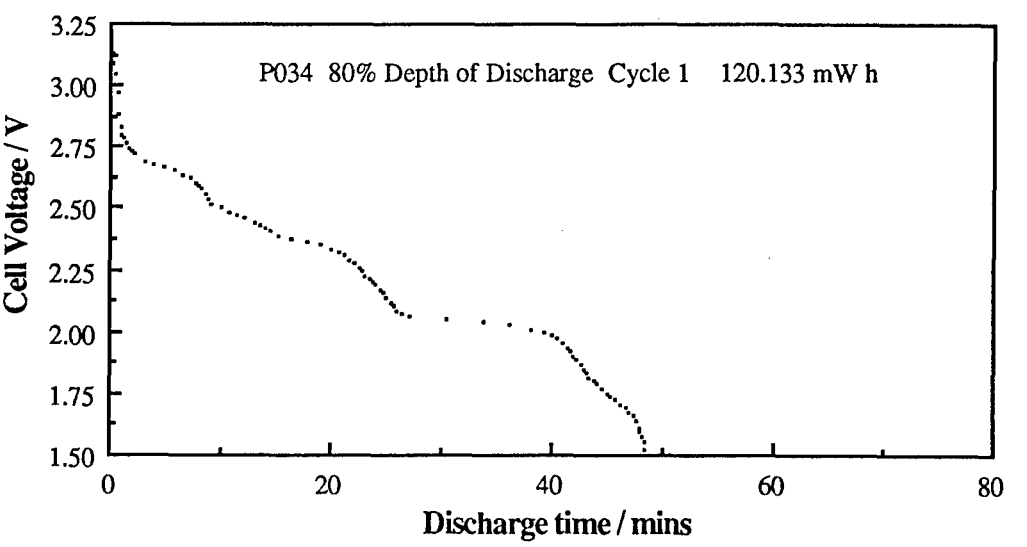
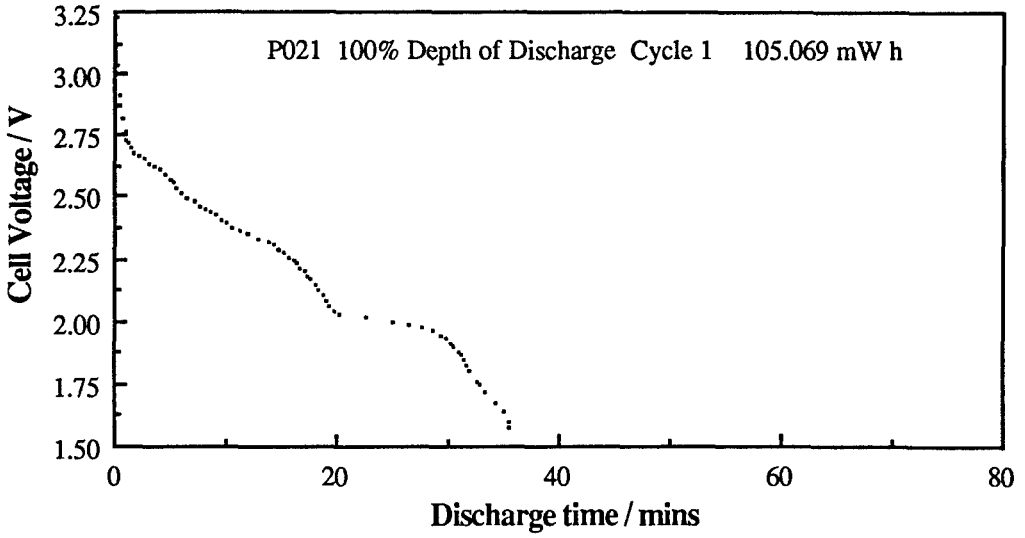
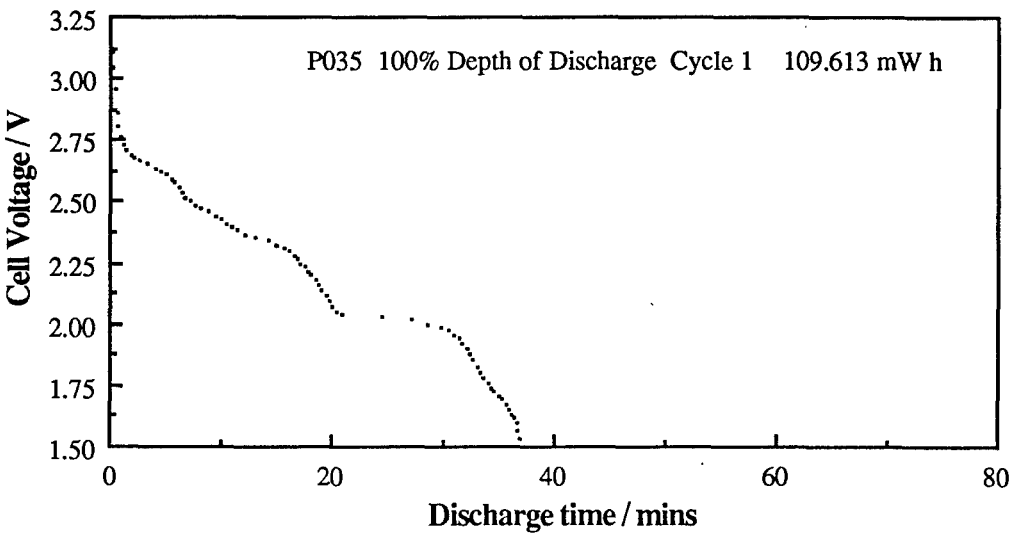


Figure 12 *First discharge data for Mark I LPB cells cycling at 80% depth of discharge.*





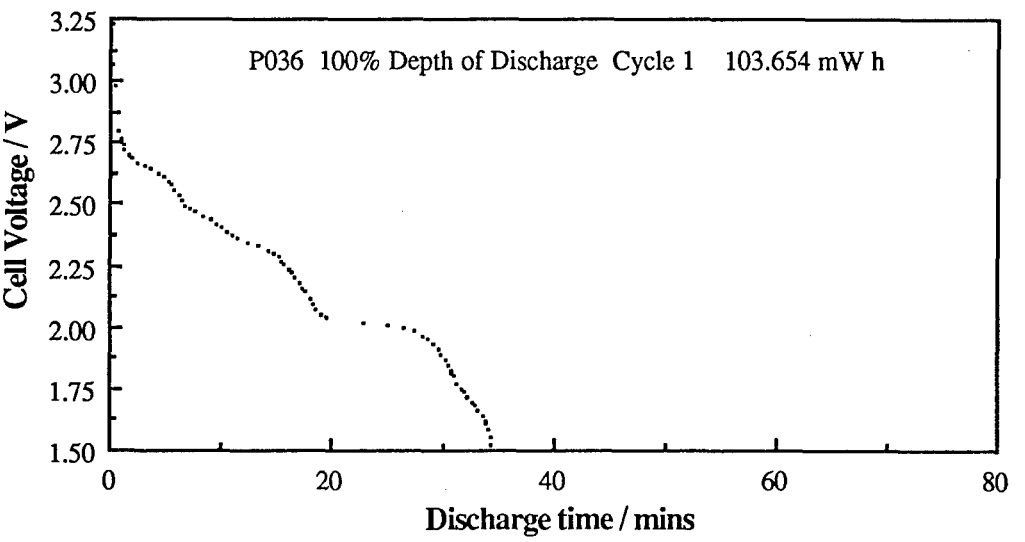


Figure 13 *First discharge data for Mark I LPB cells cycling at 100% depth of discharge.*

3. List of Publications arising from the Contract Work

AEA Technology, Harwell Laboratory has published no materials resulting from the contract work.

AEA Technology, Harwell Laboratory has no current plans to publish any of the material resulting from the contract work.

4. Professional Personnel

The following is a list of professional personnel who have contributed to the Contract Work. Dr Robin John Neat, Dr William James Macklin and Mr Raymond John Powell. None of these personnel were awarded an advanced degree during the duration of the project.

5. Interactions

No interactions between Harwell staff and any organisation, other than the Program Manager and associated staff, has taken place on the subject of the contract work during the duration of the contract.

6. Inventions and Patents

The contract work has not given rise to any inventions and AEA Technology, Harwell Laboratory has not filed or authorised others to file any patents arising from the contract work.

7. Additional Information